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by

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October 1964

EXPERIMENTAL AND THEORETICAL STUDIES
IN PLANETARY AERONOMY
Quarterly Progress Report
Covering the Period 15 July 1964 through
15 October 1964

Prepared under Contract No. NASw-840

GEOPHYSICS CORPORATION OF AMERICA
Bedford, Massachusetts 01730

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I. INTRODUCTION

This is the Fourth Quarterly Progress Report under NASA Contract No. NASw-840. This report describes the technical progress during the period from 15 July 1964 through 15 October 1964.

For convenience and ease of reference, this report is divided into four sections. In Section I, the introduction, we summarize the publications submitted or accepted for publication in accredited scientific journals as well as GCA Technical Reports generated and published during this reporting period. In Section II, the technical progress during this reporting period that falls within the categories of the Statement of Work, is described in the order in which it appears in the Statement of Work. Section III describes any additional work that was completed during the Quarter, but not necessarily required under the Statement of Work. Section IV reports miscellaneous items that are pertinent to the performance of the contract.

During the current reporting period, the following papers were submitted and/or accepted for publication or presented at scientific meetings.

1. Technical Papers submitted and/or accepted for publication in accredited scientific journals for the period 15 July to 15 October 1964

Journal

a. Submitted for Publication

Ionospheric Electron Temperatures Near Dawn
(A. Dalgarno and M. B. McElroy)

Planetary &
Space Sciences

Absorption and Photoionization Cross Sections
of CO₂, CO, A and He at Intense Solar Emission
Lines (R. B. Cairns and J. Samson)

J. Geophys. Res.

b. Accepted for Publication

Absorption and Photoionization Cross Sections
of O₂ and N₂ at Intense Solar Emission Lines
(J. Samson and R. B. Cairns)

J. Geophys. Res.
[Nov. 1, 1964]

Reactions of ¹D Oxygen Atoms in the Photolysis
of Carbon Dioxide. I (P. Warneck) [PLANETARY
PHYSICS VI]

Discussions of
Faraday Society
[No. 37, 57-65,
1964]

Reactions of ¹D Oxygen Atoms in the Photolysis
of Carbon Dioxide. II (P. Warneck) [PLANETARY
PHYSICS VIII]

J. Chem. Phys.

2. Technical Papers presented at scientific or professional meetings during this Quarter

Photoionization Threshold Potential of O₂ (J. Samson and R. B. Cairns) — Presented by J. Samson at the Seventeenth Annual Gaseous Electronics Conference, Atlantic City, New Jersey, October 14-15, 1964. (Paper A-2)

3. Published GCA Technical Reports during this Quarter

GCA TR No.

PLANETARY PHYSICS VII: Absorption and Photoionization
Cross Sections of Atmospheric Gases at Intense Solar
Emission Lines: N_2 , O_2 , CO_2 , CO, A and He (J. Samson,
R. B. Cairns and F. L. Kell  y) [September 1964]

64-13-N

PLANETARY PHYSICS VIII: Reactions of 1D Oxygen Atoms
in the Photolysis of Carbon Dioxide. II (P. Warneck)
[October 1964]

64-15-N

II. TECHNICAL PROGRESS ON ITEMS APPEARING IN THE STATEMENT OF WORK

In this section, we report only on those items that are listed in the Statement of Work. For convenience and ease of reference, each topic is discussed in the order in which it appears in the Work Statement.

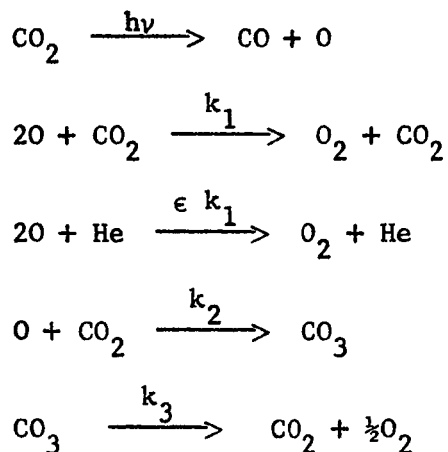
A. SOLAR PHOTOLYSIS OF PLANETARY GASES

There are four tasks listed in the Work Statement under solar photolysis of planetary gases which are designated as Items A-1, A-2, A-3 and A-4. These will be discussed in the order in which they appear in the Statement of Work.

CO₂ Photolysis at 1470 Å, 1236 Å and 1600 Å (Ref. Work Statement, Items A-1, A-2 and A-4, respectively)

In our previous QPR we defined and discussed the so-called "oxygen deficiency" associated with the photolysis of CO₂. We further showed that this deficiency could be related to at least two causes: (1) ozone formation with subsequent interaction with metal surfaces and stopcock greases and (2) the production of CO₃. Accordingly, there arose the need to reinvestigate the extent of ozone formation in the VUV photolysis of CO₂ and also to study the O₂/CO ratio as a function of various experimental parameters since this ratio can be directly related to the formation of CO₃ which could not be detected directly. Since the last Quarterly we have found that the amount of ozone formed is insufficient to account for the oxygen deficiency reflected in the O₂ quantum yields. The O₃ quantum yield was determined as $\phi(O_3) \leq 0.03$. The following results

were obtained concerning the O_2 quantum yield. The $[O_2]/[CO]$ ratio was found to depend on the light intensity, on the time interval after which an irradiated sample was subjected to analysis, and on the ratio of carbon dioxide to admixed rare gas concentration. These results are consistent with the assumption that an unstable addition compound, namely CO_3 , is formed by attachment of 1D oxygen atoms to carbon dioxide. For example, experiments in which helium was added as an inert constituent showed the $[O_2]/[CO]$ ratio to increase with the partial pressure of helium. This is expected to occur if the attachment of oxygen atoms to CO_2 is in competition with the recombination of oxygen atoms in which helium can play the role of a third body. Accordingly, the results have been interpreted by the following reaction mechanism (involving oxygen atoms in the excited 1D state):



The last reaction is included to account for the observed increase of the $[O_2]/[CO]$ ratio with time after photolysis. It has also been possible to obtain an estimate of the involved rate constants.

During the next Quarter our effort will be toward determining the rate constants more precisely and thereby aiding in obtaining a conclusive solution to the oxygen deficiency problem.

CO₂ Photolysis at 1066 Å (Ref. Work Statement, Item A-3)

The photolysis of CO₂ at 1066 Å is at best achieved by separate experimentation due to the unique experimental requirements for such a short wavelength. It is for this reason that much progress has been reported for the wavelength regions 1236 Å, 1470 Å and 1600 Å and little or no progress for the 1066 Å region. In accordance with the requirements of Item A-3 of the Work Statement, the photolysis of CO₂ at 1066 Å has been initiated during this Quarter.

B. THEORETICAL STUDIES

There are four tasks listed in the Work Statement under theoretical studies which are designated as Items B-1, B-2, B-3 and B-4. These will be discussed in the order in which they appear in the Statement of Work.

Quantum Calculations of the Photoionization Cross Sections of Atomic Oxygen Taking Account of the Individual Transitions (Ref. Work Statement, Item B-1)

This phase of the work has been completed and is described in detail in the following publications:

(a) "The Photoionization of Atomic Oxygen" [A. Dalgarno, R. Henry and A. Stewart, GCA TR No. 64-1-N and Planetary & Space Sciences 12, 235, 1964].

The Determination of Electron Temperatures in the Upper Atmosphere With Special Emphasis on the Near Sunrise Period (Ref. Work Statement, Item B-2)

During this Quarter, theoretical investigations have been completed on the determination of electron temperatures in the upper atmosphere with special emphasis on the near-sunrise period. It has resulted in the submission of a paper entitled "Ionospheric Electron Temperatures Near Dawn" by A. Dalgarno and M. B. McElroy. The scientific content of this paper is included here.

Solar ultraviolet radiation leads to a source of energy which preferentially heats the ionospheric electrons and maintains the

electron temperature T_e above the neutral particle temperature T_g . It has been suggested that near dawn, when the ambient electron densities n_e are small, the electron temperature may be anomalously large; calculations of the location and extent of the anomaly have been performed and are discussed below.

The local heat source Q may be computed following standard procedures and values of Q at altitudes of 200, 250, 300, 350 and 400 km in an atmosphere with an ionospheric temperature of 750°K are listed in Table 1 for a number of solar zenith angles θ .

Table 1

Values of Q ($\text{keV cm}^{-3} \text{ sec}^{-1}$)

h	$\theta=90^\circ$	$\theta=89^\circ$	$\theta=87^\circ$	$\theta=80^\circ$	$\theta=60^\circ$
200	0.1	0.1	0.2	1.0	3.5
250	0.3	1.0	1.5	2.6	3.7
300	0.7	1.0	1.1	1.3	1.4
350	0.4	0.5	0.5	0.5	0.5
400	0.2	0.2	0.2	0.2	0.2

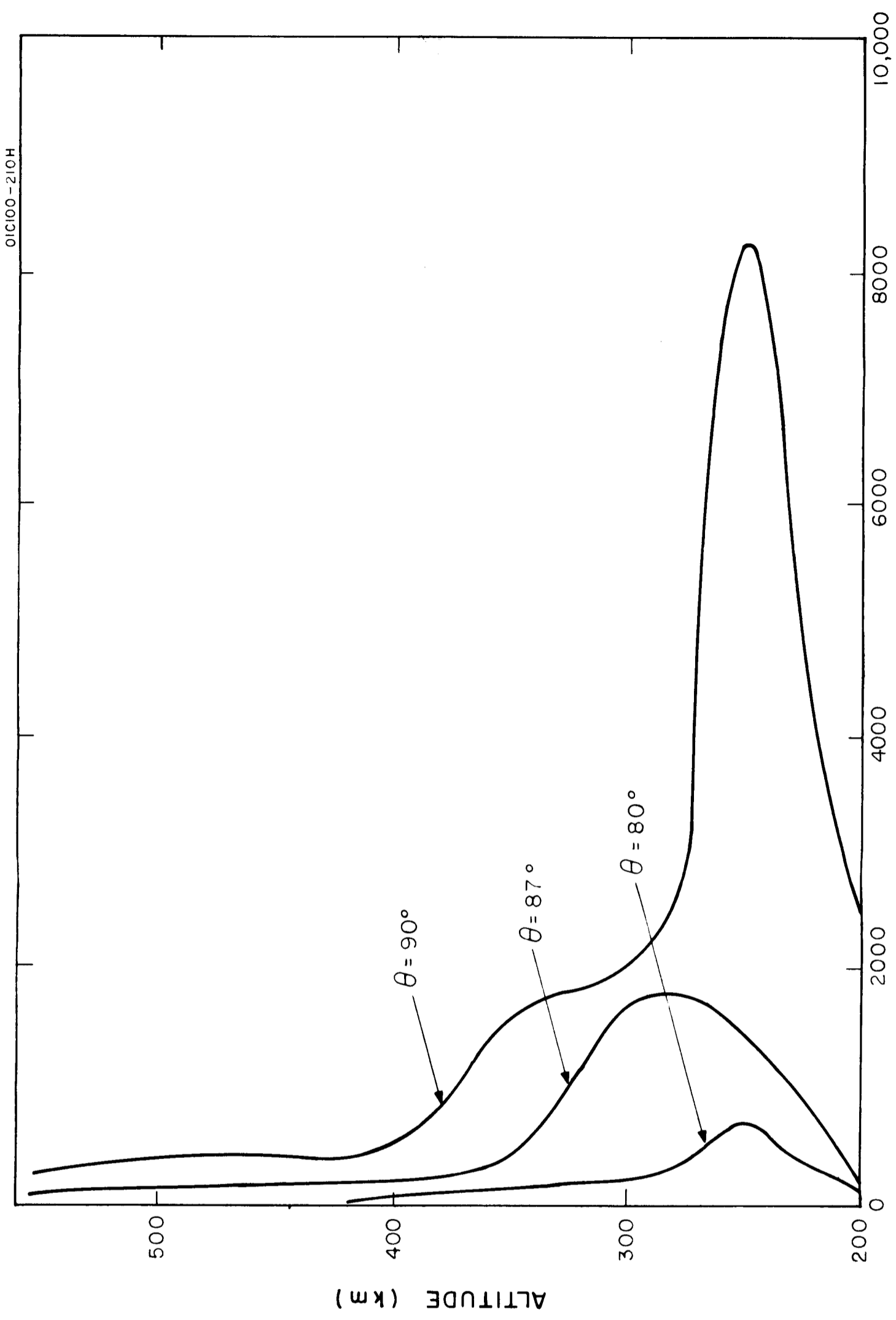
The heated electron gas cools in collisions with the neutral particles and positive ions, the most important processes being elastic scattering by positive ions, rotational and vibrational excitation of molecular nitrogen

and excitation of atomic oxygen to the 1D level. The calculated variation of the cooling efficiency with electron temperature shows that at low altitudes, collisions with molecular nitrogen control the cooling for all electron temperatures; whereas at high altitudes, cooling by collisions is due to (a) elastic scattering by positive ions where T_e is small and to (b) excitations of atomic oxygen where T_e is large.

The equilibrium electron temperature is obtained by equating the rate of heating to the rate of cooling. The value so derived is very sensitive to the assumed ambient electron density n_e , the controlling parameter being Q/n_e at low altitudes and Q/n_e^2 at high altitudes, and the variation of T_e after sunrise will be governed more by changes in n_e than by the changes in Q .

We shall assume arbitrarily that the electron density in the ionosphere changes linearly from the nocturnal profile measured by Sagalyn and Smiddy to the daytime profile derived by Hanson as θ changes from 90° to 80° . The actual situation is much more complicated and our results, presented in Figure 1, serve merely to illustrate the possible behavior of T_e . They suggest that very high values of T_e may occur at 250 km for a short interval following sunrise. Essentially, this behavior has been found by Sagalyn and Smiddy in the Discoverer satellite data.

Cooling by excitation of atomic oxygen is important and the high values of T_e will be accompanied by a glow in the oxygen red lines at 6300 \AA . The predicted intensity corresponding to the model of T_e shown



$T_e - T_g$ (°K)

Figure 1.

in Figure 1 varies from 500 Rayleighs at 90° to 1 Rayleigh at 80° . There are other processes which populate the 1D level of atomic oxygen but a red dawn flash due to the high electron temperatures might be observable. Excitation of the vibrational levels of molecular nitrogen also contributes to the cooling of the hot electron gas and this should be reflected in an enhanced vibrational development of the first negative band system.

It can be shown that with increasing altitude a maximum and a minimum are introduced into the curve of cooling efficiency against temperature. Hence if Q is large enough at high altitudes, the electron temperature may run away from an equilibrium controlled by collisions with positive ions to one controlled by collisions with neutral particles. Thus, with our model, if at 650 km Q/n_e^2 were to increase through $6.8 \times 10^{-9} \text{ eV cm}^3 \text{ sec}^{-1}$, $T_e - T_g$ would change from 1500°K to over 5000°K and if Q/n_e^2 were to decrease through $6.2 \times 10^{-9} \text{ eV cm}^3 \text{ sec}^{-1}$, $T_e - T_g$ would change from 4000°K to 800°K . Such a heat source cannot be supplied by the local deposition of energy from solar ultraviolet radiation. However, Hanson and Mariani have pointed out that the faster photoelectrons escape and they must be a significant source of heat at great altitudes. According to our calculation of the production of fast electrons by solar ultraviolet radiation, the upward flux at dawn approaches $10^{10} \text{ cm}^{-2} \text{ sec}^{-1}$ which exceeds the critical value where n_e is less than about 10^5 cm^{-3} . Cooling by thermal conduction prevents the electrons from attaining the very high temperatures that would otherwise result at great altitudes

from the flux of fast photoelectrons, but the tendency of the electron temperature to run away should be observable at dawn. An estimate of the duration of the effect will require the solution of the time-dependent problem.

We have assumed in this discussion that the positive ion temperature T_i is equal to the neutral particle temperature T_g . In fact, the heating effect of the escaping photoelectrons will cause T_i to exceed T_g .

This investigation satisfies the requirement of Item B-2 in the Work Statement; thus, this phase is now also completed.

Determination of the Cooling of Electrons by Rotational Excitation of Molecular Nitrogen in the D-Region (Ref. Work Statement, Item B-3)

This study on the determination of the cooling of electrons by rotational excitation of molecular nitrogen in the D-region has now been initiated and progress will be reported in the next QPR.

The Improved Calculations of the Ambi-Polar Diffusion Coefficient Appropriate to the F-Region (Ref. Work Statement, Item B-4)

This phase of the work has been completed and is described in detail in the following publication:

(a) "Ambipolar Diffusion in the F-Region" [A. Dalgarno, J. Atmos. Terrest. Phys., to be published].

C. EXPERIMENTAL INVESTIGATIONS IN THE VUV (1000-2000 Å) AND EUV
(BELOW 1000 Å)

There are four tasks listed in the Work Statement under experimental investigations of the EUB and VUV which are designated as Items C-1, C-2, C-3 and C-4. Each task is discussed in the order in which it appears in the Statement of Work.

Measurement of Absorption and Photoionization Cross Sections in the VUV and EUV Regions for O₂, N₂ and A (Ref. Work Statement, Item C-1)

This phase of the work has been completed and is described in detail in the following publications:

(a) "Absorption and Photoionization Cross Sections of O₂ and N₂ at Intense Solar Emission Lines" [J. Samson and R. B. Cairns, J. Geophys. Res., 1 Nov 1964];

(b) "Absorption and Photoionization Cross Sections of CO₂, CO, A and He at Intense Solar Emission Lines" [J. Samson and R. B. Cairns, J. Geophys. Res., 1 Jan 1965];

(c) "Experimental Photoionization Cross Sections in Argon from Threshold to 280 Å" [J. Samson, GCA TR No. 64-3-N and J. Opt. Soc. Amer., 54, 420, 1964];

(d) "Photoionization of the Rare Gases" [J. Samson, GCA TR No. 64-3-N];

(e) "Absorption and Photoionization Cross Sections of Atmospheric Gases at Intense Solar Emission Lines: N_2 , O_2 , CO_2 , CO, A and He [J. Samson, R. B. Cairns and F. L. Kelley, GCA TR No. 64-13-N, Sept 1964].

Laboratory Measurements of Absorption and Photoionization Cross Sections of Atomic Oxygen, Atomic Nitrogen and Atomic Hydrogen (Ref. Work Statement, Item C-2)

Measurements of the photoionization cross sections of atomic hydrogen, oxygen and nitrogen are of fundamental importance both for ionospheric studies and for comparison with theoretical estimates. Of greatest interest are the cross sections of atomic oxygen. Calculations of these cross sections have been made by several authors but no reliable experimental determinations have been made to date.

The cross sections of atomic nitrogen have been crudely measured between 800 Å and 400 Å by Ehler and Weissler who measured the absorption of monochromatic radiation by nitrogen atoms produced in a Philips ionization gauge type gas discharge. The atom concentration was not directly measured and as a consequence, the data were open to several interpretations. In the present work, a more reliable approach has been adopted. This report describes, briefly, the technique and present progress.

The photoionization threshold of O is 910.4 Å and that of O_2 is greater than 1025 Å. Since it is not possible to completely dissociate molecular oxygen, the simultaneous absorption by both O_2 and O has to be accounted for. This has been done but the details are not given here.

Two outstanding problems associated with the current investigation are (a) the method of producing atomic oxygen and (b) the measurement of the atom concentration.

(a) Method of Producing Atomic Oxygen

A microwave electrodeless discharge produced only 5 percent dissociation of O_2 at a total gas pressure of 0.5 mm Hg when the gas was not dried. (It is well known that the degree of dissociation in dry O_2 is negligible.) An attempt to promote dissociation by increasing the partial pressure of water vapor in the gas prior to dissociation and removing it in a dry ice acetone trap after dissociation was not successful. Further, it was found that the addition of a second microwave discharge either in series or in parallel with the first did not increase the degree of dissociation by more than 10 percent.

Next, a radio frequency generator of output 20 kW at 450 kc, full load, was used. We noted that it could not be used at maximum power since this punctured the walls of the quartz discharge tube. Even after many adjustments of the electrode geometry and transformer coupling, the degree of dissociation obtained did not exceed that produced by a single microwave discharge by more than 50 percent.

To try alternate methods, an rf generator of lower power output operating at 25 Mc has been constructed but not as yet employed.

In the above attempts, a 3-percent addition of H_2 was found to increase the degree of dissociation from 3 percent to 17 percent. However, such a large addition of H_2 increased the rate of volume recombination to such an extent that there was a large atom concentration gradient along the absorption cell. In order to determine the number of absorbing atoms per cm^2 -column, therefore, this gradient would have to be accurately measured. The addition of H_2 creates another difficulty in that OH and H_2O are generated and their absorptions cannot be satisfactorily taken into account in the present design.

Finally, an 80-percent He, 20-percent O_2 mixture at a total gas pressure of 0.75 mm Hg yielded 24 percent dissociation of O_2 . Helium is transparent to radiation of wavelengths longer than 504.3 \AA and below this wavelength the cross sections are known so that it is a suitable additive and offers no particular complications. This mixture appears to offer the best available for this experiment.

For the detection of extreme ultraviolet radiation, one end of the absorption cell has to be coated internally with sodium salicylate. It has been shown that O atoms do not recombine rapidly on the sodium salicylate surface. It is not yet known whether active species affect the quantum efficiency of the sodium salicylate.

(b) Measurement of the Atom Concentration

The NO_2 titration technique has been extensively studied and seems to be capable of measuring the atom concentration with about a

5 percent accuracy. In fact, this technique was used to measure the degree of dissociation when H_2 and He were added to O_2 and is being used in the final experiment.

A Wrede-Harteck Gauge has also been used and will ultimately be useful in the measurement of atomic hydrogen cross sections where the titration technique is less accurate.

With these two major problems behind, the final apparatus has been designed to attach to the $\frac{1}{2}$ meter Seya Monochromator. The shop construction has begun and the final assembly and test should be achieved within the next Quarter.

Laboratory Measurements of the Kinetic Energies of Photoelectrons
From N_2 and O_2 (Ref. Work Statement, Item C-3)

Several design criteria were compared in order to establish the optimum choice for a suitable electron energy analyzer for measuring the photoelectron energies. The selected analyzer was designed as reported in the last Quarterly Progress Report. During the present Quarter, it has been drawn up and actual construction has been completed by our Model Shop. The next task is to test this analyzer. It is planned to give a complete description of the analyzer and its operating characteristics in the next QPR.

The Mass Analysis of the Products of Photoionizing O_2 , N_2 and CO_2
Below 1000 Å (EUV) (Ref. Work Statement, Item C-4)

This item has received little attention thus far due to the efforts on Items C-1, C-2 and C-3. However, some effort has been given to a systematic comparison between several alternate mass spectrometers to determine the optimum type to unite with the Seya UV monochromator.

D. THEORETICAL AERONOMY

There are five tasks listed in the Work Statement under theoretical aeronomy which are designated as Items D-1, D-2, D-3, D-4 and D-5. Each task is discussed in the order in which it appears in the Statement of Work.

Photoionization Rates for Constituents of the Atmospheres of Mars and Venus (Ref. Work Statement, Item D-1)

For the calculations of the photoionization rates of constituents in the Martian atmosphere, a model atmosphere is required. We are now in a position (see Item D-2 below) to suggest an acceptable model for the composition in the upper atmosphere of Mars so that the required calculations can now be performed. This phase is now only in the beginning stage but progress is as expected.

As yet, no acceptable model is available for the atmosphere of Venus so that these calculations have not been attempted to date.

CO₂ Photolysis in the Atmospheres of Mars and Venus (Ref. Work Statement, Item D-2)

Considerable effort has been directed towards determining the distribution of the photolysis products in the upper atmosphere of Mars. Employing a wide range of models, we now have what we believe to be a usable model of the Martian atmosphere. The distributions have been calculated for the following species: CO₂, CO, O₂, O₃, O, N₂ and A. Our model can now be employed for the performance of Item D-1 above.

It is anticipated that within the next Quarter, results of this phase will be published as a GCA Technical Report. Concerning Venus, in spite of the lack of good data, we will apply the same techniques to that planet as we have to the Martian atmosphere in order to obtain at least a working model for the completion of Item D-1 above.

The Role of Cosmic Dust Deposited in the Upper Atmospheres of Earth, Mars and Venus (Ref. Work Statement, Item D-3)

In the last Quarterly Progress Report our numerical integration scheme was described. It was tested and found to agree with the closed form solutions, thereby proving it to be applicable to the physical model described in GCA TR No. 63-4-N. This numerical scheme affords far greater flexibility than the closed form solutions for the choice of: (a) the source function (the cosmic dust deposition rate as a function of altitude); (b) the variation and magnitude of the diffusion coefficient with altitude; and finally (c) the physical chemical behavior of the vaporized debris as a function of altitude and deposition rate. Since the last Quarter, we have progressed significantly towards determining the proper functions for parameters (a) and (b), the source function and diffusion parameters, respectively. A brief description of these follows:

(a) Source Function

Recently, a number of authors arrived at estimates of the terrestrial accretion of meteoric matter as a function of particle mass. We now require some way of determining what percentage of this

mass influx vaporizes, and hence contributes to the neutral atomic species in the upper atmosphere.

Certain crude methods are available; for example, in our previous work on meteor vaporization we employed Whipple's theory [1957] to determine the maximum particle size that will just survive atmospheric passage for any given velocity. Those studies showed that only a small percentage of the mass influx would vaporize. On the other hand, in order to calculate the deposition rate of those particles that did vaporize, we used Herlofsen's method. While both theories assume free molecular flow and both assume the same model of energy transfer from air molecules to micrometeorites, there are basic differences. Whipple neglects the heat capacity of the micrometeorite assuming that energy introduced into the particle raises its surface temperature immediately. Herlofsen assumes an atmosphere in hydrostatic equilibrium and further assumes that vaporization begins as soon as the particle enters the atmosphere.

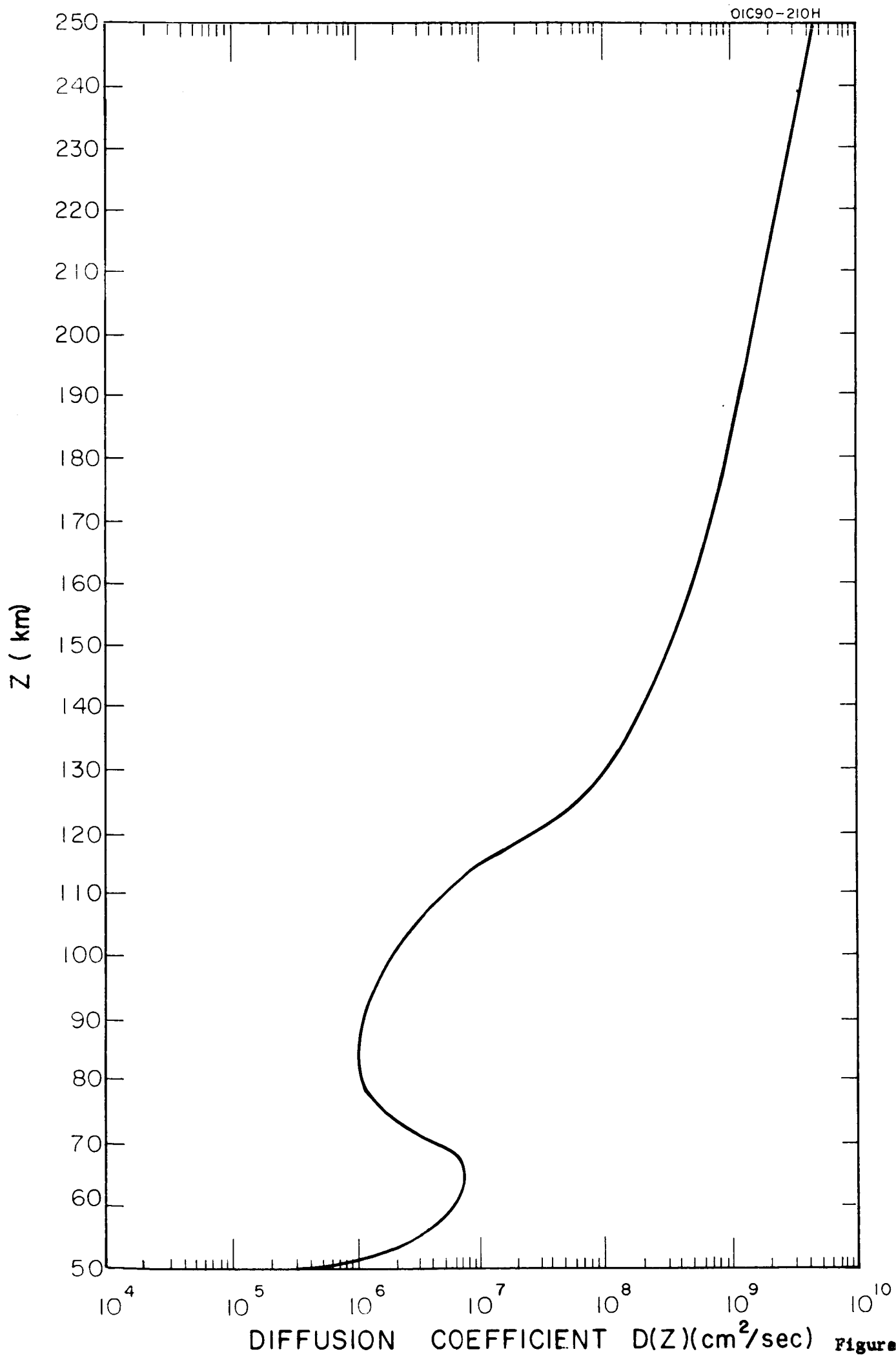
In order to arrive at a consistent model and to establish criteria for survival or vaporization, we have chosen to integrate the equations of motion of the micrometeorite. Our model assumes that the entire process occurs under conditions of free-molecular flow. The particle is assumed to have a finite heat capacity and to radiate with a grey-body emissivity. We assume that vaporization begins once the particle reaches its melting temperature. Our model atmosphere for the calculation is the 1962 Standard Atmosphere.

The necessary computer program has been compiled and test cases are now being processed. Preliminary results indicate significant differences with our previous model. There is, however, no guarantee that this model will necessarily prove to be adequate for the present purpose.

During the next reporting period, we will continue our efforts to develop and test this model to estimate more accurately, if possible, what percentage of the mass influx does vaporize and to determine, if possible, the resulting vaporization as a function of height in the model atmosphere.

(b) Diffusion Coefficient With Altitude

For altitudes above 80 km we have chosen to employ the measured diffusion coefficients as achieved under Contract No. NAS5-215, in which sodium and other alkali metals are released into the upper atmosphere, and by proper analysis diffusion coefficients are determined. Unfortunately, for altitudes below 80 km there are no reliable experimental values; in fact, even the nature of the diffusion is not well established. However, since the data are required, we have used the equations of H. Lettau to calculate theoretical values for these altitudes. It turns out that the experimental (80-250 km) and theoretical (below 80 km) data agree in the vicinity of 80 km so that no normalization was necessary. Accordingly, we are left with a smoothly varying curve to indicate the diffusion coefficient as a function of altitude. This is shown in Fig. 2. This is the curve to be employed for studies in the Earth atmosphere.



(c) Physical Chemical Behavior of the Vaporized Debris

For a complete study of this current problem one must consider the subsequent physical, chemical and dynamic behavior of the vaporized species after it is deposited in the upper atmosphere. The interplay of several processes makes it difficult to generate a realistic model. To date, the various processes have been defined and crude estimates have been attempted in order to simplify the problem to some degree. The complete solution may not be tractable, but by constant application of physical reasoning we feel confident that a workable model can be generated and finally incorporated into the present scheme. Once these parameters are defined, final calculations can be performed.

Concerning this over-all problem of cosmic debris, it is interesting to note that recently, R. S. Narcisi and A. D. Bailey have reported on the results obtained with a quadrupole mass spectrometer flown from 64 km to 112 km in the Earth's atmosphere. Six new positive ion peaks appeared abruptly above 82 km; the authors suggest that these are due to the metallic ions of sodium (23^+), magnesium (24^+ , 25^+ and 26^+) and calcium (40^+). In addition, the maximum concentrations are found in the vicinity of 95 km. These data are compatible with the present cosmic debris model as described in GCA TR No. 63-4-N.

The Intensity of N_2^+ , O_2^+ and O^+ Visible Radiation Arising From Fluorescence of the Solar Ultraviolet (Ref. Work Statement, Item D-4)

The intensity of radiations arising from fluorescence of the solar UV was first reported in QPR No. 4 under NASA Contract No. NASw-395. That

preliminary work showed that if the radiation is in the visible and its intensity large enough, a new method can be suggested for monitoring variations in the solar UV radiation from the Earth and thereby relate these to solar activity. However, a more quantitative study was indicated. This is the main objective of the present study which is to continue where the former study left off. It is anticipated that this work will be completed before the end of the current contract.

Quantum Calculations on the Transition Probabilities of Lines of O, N, O⁺ and N⁺ (Ref. Work Statement, Item D-5)

This phase of the work has been completed and is described in detail in the following publications:

(a) "An Expansion Method for Calculating Atomic Properties - I. The 2S and $^2P^o$ States of the Lithium Sequence" [M. Cohen and A. Dalgarno, GCA Technical Report No. 64-5-N].

(b) "An Expansion Method for Calculating Atomic Properties - II. Transition Probabilities" [M. Cohen and A. Dalgarno, GCA Technical Report No. 64-6-N and Proc. Roy. Soc. A280, 258, 1964].

E. LUMINOSITY OF PLANETARY GASES

There are seven tasks listed in the Work Statement under luminosity of planetary gases which are designated as Items E-1, E-2, E-3, E-4, E-5, E-6 and E-7. Each task is discussed in the order in which it appears in the Statement of Work.

The Measurement of the Rayleigh Defect Below 2000 Å (Ref. Work Statement, Item E-1)

See Item E-2 below.

The Measurement of Scattering Cross Sections at Lyman-Alpha and Other Wavelengths for the Rare Gases, Molecular Hydrogen and Nitrogen (Ref. Work Statement, Item E-2)

We are in the process of preparing a GCA Technical Report describing the laboratory measurements for obtaining the scattering cross sections of argon, nitrogen, neon, hydrogen and helium. The results will be presented at the meeting of the American Physical Society in Chicago, October 23, 1964 (Paper No. D-13). As a final task, the light source employed has been checked on the monochromator to establish that it was indeed monochromatic. This was found to be the case.

Considerable progress has been made in the design and construction of new experimental equipment for deriving experimental scattering cross sections by attenuation measurements at high pressures. This unique technique for obtaining these data will be described more fully in the

next Quarter after some effort has been given toward checking out and testing the new apparatus.

Fluorescence Radiation of O_2 , N_2 and CO_2 (Ref. Work Statement, Item E-3)

When solar ultraviolet radiation ionizes an atmospheric constituent, some of the radiation is absorbed into the excited electronic levels of the ion which may then radiate in the visible. For example, the first negative and the Meinel bands of nitrogen have been observed in the upper atmosphere. Emissions from O_2^+ and O^+ have also been associated with upper atmospheric phenomena. In spite of the importance of these areas of research, very little laboratory results have been obtained on the fluorescence radiation from planetary gases. The required quantitative data can only be obtained by means of a systematic laboratory study. Preliminary work on this program in our laboratory has already indicated that such experiments are feasible in the GCA VUV laboratory. For example, recent measurements in this laboratory have identified the onset of the first negative bands and the second negative bands at 683 \AA and 734 \AA , respectively. The results are quantitative and serve to verify the feasibility of such experiments. We plan to use an experimental technique which has not as yet been employed in which we hope to obtain the discrete spectra associated with the first negative bands and the second negative bands. No detailed description is given here as yet since this work is in its preliminary stage.

Measurement of Scattering Cross Sections in the Vicinity of
Resonance Lines (Ref. Work Statement, Item E-4)

The present scattering setup is not suitable for this phase. In fact, this experimental task can best be performed along with the new "attenuation" technique mentioned under Item E-2. Accordingly, accumulation of any pertinent data will have to wait for the development of that system.

Spectral Reflectivity and Luminosity of the Atmospheres of Mars,
Earth and Venus (50 Å Bandwidths for the Region Below 2000 Å)
(Ref. Work Statement, Items E-5, E-6 and E-7)

The spectral reflectivity and luminosity for the atmospheres of Mars and Earth have been completed for 50 Å bandwidths for the region below 2000 Å (see QPR No. 3). The necessary calculations to obtain the 1 Å resolution and to extend the calculations to 3000 Å have not been attempted as yet. However, no difficulty is expected since it is only a matter of some time, effort and proper programming on the IBM 1620.

The calculations for Venus have still not been performed since a satisfactory model is still not available. When it does become available (see Item D-1), the 1 Å resolution calculations will be performed directly along with those for Mars and Earth. The calculations that we have been discussing include the roles of scattering and absorption only. To date, there has been no effort to include the effective airglow, chemiluminescence, fluorescence and resonance radiation in planetary atmospheres.

III. ADDITIONAL WORK

During the performance of a contract of this nature, one is necessarily influenced by the appearance of new data and theories. Often it is a relatively simple task to make significant contributions with either some additional effort or as a fallout from a current study. As a result, data are obtained over and above those required in the performance designated in the Work Statement. During this Quarter, additional work has been performed on the following problems: (A) Absorption characteristics of the Earth's atmosphere for the strong solar emission lines below 1000 \AA ; (B) the relationship between the presence of ozone and oxides of nitrogen in the Martian atmosphere; (C) Rayleigh scattering by helium and (D) Photoionization threshold for O_2 .

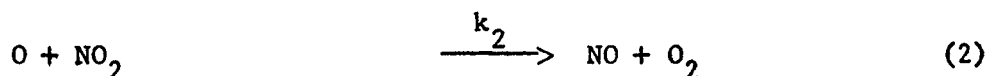
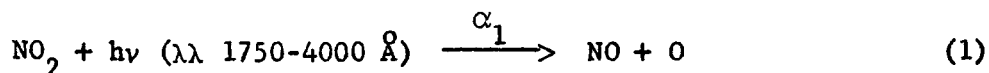
A. ABSORPTION CHARACTERISTICS OF THE EARTH'S ATMOSPHERE FOR THE STRONG SOLAR EMISSION LINES BELOW 1000 \AA

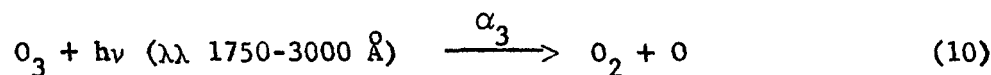
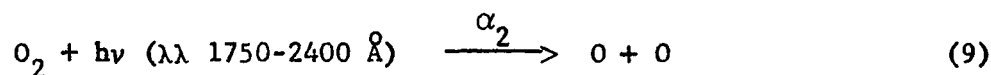
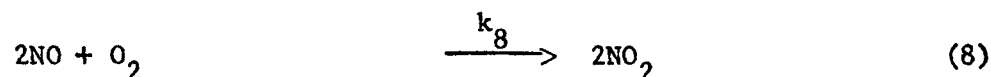
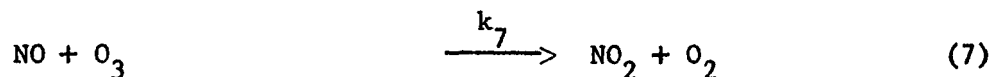
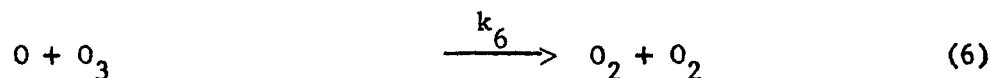
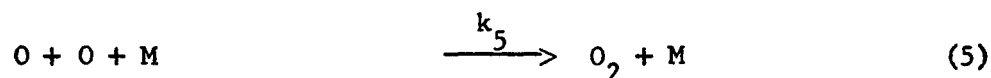
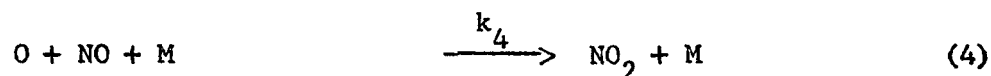
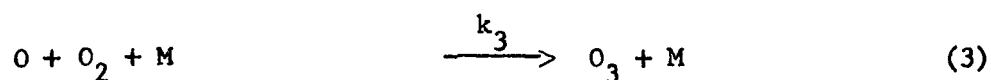
We are currently investigating the optical properties of the model atmosphere proposed by Hinteregger at the COSPAR Meeting this year. The investigation is concerned with the absorption characteristics of the atmosphere for the strong solar emission lines below 1000 \AA . The pertinent cross sections have been measured recently by Samson and Cairns under this contract and have been published as GCA Technical Report No. 64-13-N. The only cross sections available for atomic oxygen are theoretical values; the most recent of these have been published by Dalgarno, Henry and Stewart under this contract as GCA Technical Report No. 64-1-N.

During the next reporting period we will calculate the optical thickness of the Hinteregger model as a function of altitude for each of the strong solar emission lines.

B. THE RELATIONSHIP BETWEEN THE PRESENCE OF OZONE AND OXIDES OF NITROGEN IN THE MARTIAN ATMOSPHERE

The importance of the role of photodecomposition of NO_2 in the Martian atmosphere was emphasized in the previous report. In the steady-state conditions of solar illumination for the photochemistry of NO_2 it is found that there is a correlation between NO_2 , NO and O_2 . With the available limits of $\text{O}_2 = 70 \text{ cm-atm}$ [L. D. Kaplan et al., *Astrophys. J.* 139, 1, 1964] and $\text{NO} = 87 \text{ cm-atm}$ [Carl Sagan, 1964 - private communication], the amount of NO_2 is less than 0.1 mm-atm which is insufficient to account for the "Martian blue haze." At this stage, the other minor constituents such as O_3 , NO_3 , N_2O_5 , etc., were calculated and it was found that O_3 can be only a very minor constituent in the presence of oxides of nitrogen as compared to the permissible amount in the absence of nitrogen oxides (for the same oxygen content). Thus, there exists an important relationship between the concentrations of NO_2 and O_3 such that the permissible O_3 -content must decrease sensitively with increasing amounts of NO_2 . To investigate this interesting correlation between NO_2 and O_3 , a detailed study of the photochemistry of an oxygen-nitrogen system in the Martian atmosphere has been undertaken. This study is essentially the combined study of the photochemistry of NO_2 and O_3 and is comprised of the following ten reactions:





The details of computations are not given here since they will appear in a forthcoming GCA Technical Report on this subject. However, it is worth mentioning that our calculations are confined to the ground level of the Martian atmosphere for steady-state conditions under solar illuminations. From this study, the following interesting conclusions may be drawn:

- (1) The concentration of ozone decreases with increasing amounts of nitrogen dioxide.
- (2) If only 0.01 mm-atm nitrogen dioxide is present, the amount of ozone must be negligible. Alternatively, for a significant amount of ozone to be present, only negligible amounts of oxides of nitrogen, i.e. NO and NO₂, can be permitted.

- (3) The upper limit of NO_2 can be maintained only if the amount of nitric oxide simultaneously present is several orders of magnitude greater than NO_2 and this amount will be much greater than the limit of $\text{NO} = 87 \text{ cm-atm}$ given by Sagan [1964].

C. RAYLEIGH SCATTERING BY HELIUM

Under the current experimental program we have been successful in obtaining the Rayleigh scattering cross section by helium at Lyman-alpha (see Item II-E-2). Since this is the only measurement of its kind to date, it would be of significant value to compare the results with theory. Accordingly, a new technique was developed to make refined theoretical calculations to determine the Rayleigh scattering by helium (including the value at Lyman-alpha for direct comparison with our experimental value). The computations are still in progress but preliminary results already suggest that there will be excellent agreement between the measured and theoretical values, at least at Lyman-alpha. The detailed calculations are not given here since they will be incorporated in a forthcoming GCA Technical Report.

D. PHOTOIONIZATION THRESHOLD FOR O_2

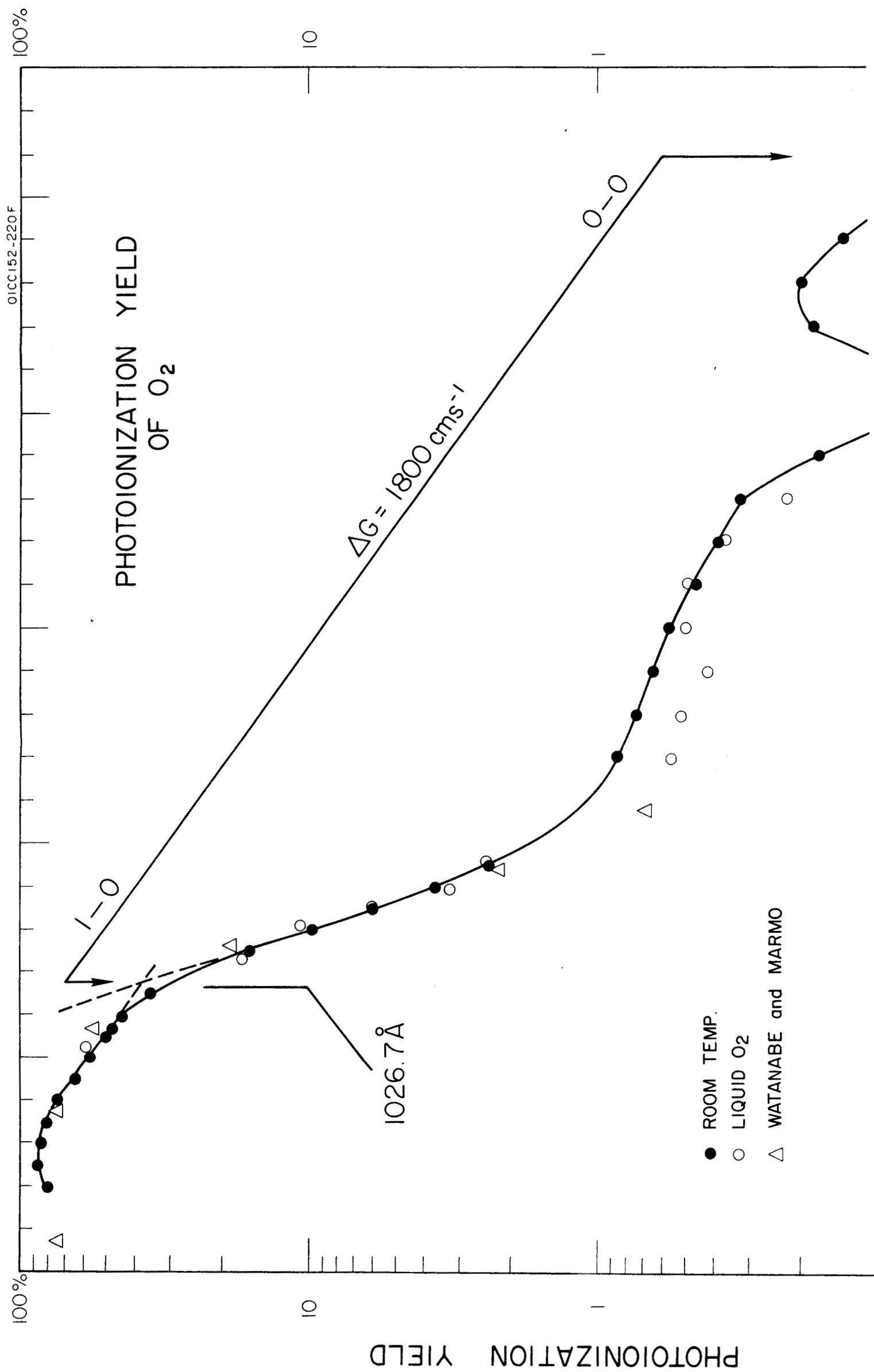
The investigation described was performed along with the investigation of photoionization cross sections of O_2 . Apparently, the ionization potential (IP) of O_2 is not precisely known since the present work and the earlier work of Watanabe and Marmo show that ions are formed by radiation around 1030 \AA in spite of the fact that the presently accepted value of the IP is at 1026.5 \AA . It is clearly important to determine the true IP since the solar spectrum contains at least three lines of comparable intensity in the vicinity of the presently accepted threshold value; namely, HI 1025.7 \AA , OVI 1032 \AA , and OVI 1038 \AA . Some theories of the ionosphere have stressed the importance of the Lyman-beta line at 1025.7 \AA as controlling the base of the E-region — but does this wavelength ionize O_2 ? Thus, what is the true IP of O_2 ?

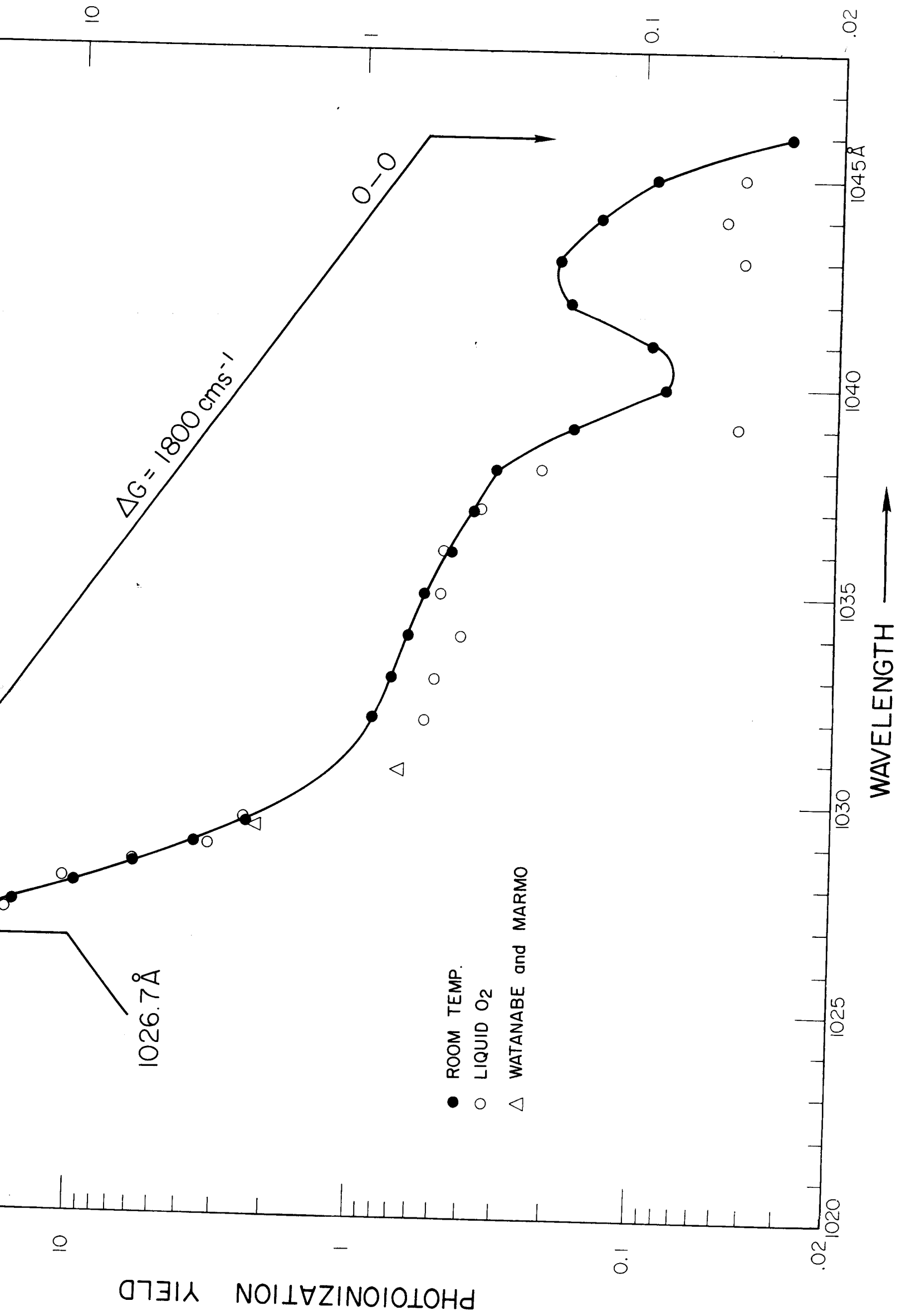
The first photoionization threshold measurements for O_2 were made by Watanabe and Marmo who obtained a threshold wavelength of 1026.5 \AA by locating what they believed to be the (0-0) transition. However, due to the difference in internuclear separation of the atoms in the neutral and ionized molecule, the (0-0) transition is very improbable. It is finite, however, and a plot of the photoionization probability should show a step function at the (0-0) transition and again at the (1-0) transition. Watanabe applied this explanation to the case of O_2 and ascribes the observed first break in the ionization curve as the (0-0) transition, representing the true IP of the molecule. It so happens

that this value is in excellent agreement with Mulliken's theoretical value and also with that obtained by electron impact methods. However, ions appear at lower energies than the suggested IP which cannot be due to ionization of molecules in high rotational levels since the selection rules preclude this. Nevertheless, the IP is lowered for molecules in higher vibrational states; but at room temperature, only 6×10^{-2} percent of the molecules are in the first vibrational state. In spite of this, with sufficient sensitivity it is possible to observe ions due to photoionization of these vibrational states. On the other hand, at liquid N_2 temperatures the population of the first vibrational state is only 2×10^{-11} percent of the ground state population - a factor of 10^9 less than at room temperature. Thus, if ions are observed at the threshold at room temperature, they certainly should disappear at liquid N_2 temperatures and the probability curve should indeed be a step function. This was checked in the present investigation.

Employing the $\frac{1}{2}$ -meter Seya monochromator with a 1 \AA bandpass and a DC hydrogen discharge lamp, the threshold wavelength range (from 1020 \AA to 1050 \AA) was studied.

An ionization chamber was constructed which was surrounded by an outer jacket containing liquid oxygen. With this setup, the ionization yields of O_2 were measured first at room temperature and then at liquid oxygen temperature in the wavelength region $1020 - 1050 \text{ \AA}$. Figure 3 is a plot of photoionization yield as a function of wavelength. The solid data points represent the results at room temperature which should be compared





to the triangular data points of Watanabe and Marmo also obtained at room temperature. When their data are plotted on a semilog scale, an abrupt change in slope is apparent; Watanabe et al. ascribed this change to the (0-0) transition and hence to the true IP. If this were the case, however, those ions observed at the longer wavelengths would disappear at liquid O₂ temperatures. As can be seen, the ions do not disappear even out to the largest wavelengths. Thus, the true IP must be at least 1046 Å. Further, the energy difference between 1046 Å and 1026 Å (the break in the slope) corresponds almost exactly to the energy separation between the zero and first vibrational states of O₂⁺; namely, 1843 cm⁻¹. Thus, we interpret the 1026 Å break as being due to the (1-0) transition. Subtracting the vibrational energy of 1843 cm⁻¹, we obtain the IP at 1047.2 Å (11.84 eV).

The effect of this new value on the Earth ionosphere is currently being evaluated.

IV. MISCELLANEOUS INFORMATION

In this section is included any information not yet discussed which is pertinent to the performance of the current contract.

On October 7 and 8, Drs. Samson and Cairns attended the meeting of the Optical Society of America in New York City in order to meet with colleagues in the field of ultraviolet spectroscopy. During this meeting a special session was devoted to this field so that many of the prominent scientists in this area were in attendance. The discussions with colleagues proved to be extremely valuable to our current work on planetary atmospheres and probably saved us about one month of fruitless research. These discussions were aimed primarily at the techniques to measure atomic oxygen cross sections.

An important part of our program has been to measure the photoionization cross sections of O_2 ; however, the ionization threshold for O_2 is not known with any precision. The currently accepted value is at 1026.5 \AA . This is sufficiently close to the important solar line at 1025.5 \AA (Lyman-beta) so that some scientists have questioned its ability to contribute to the ionosphere. Our present research has indicated a lower ionization potential closer to 1040 \AA . Drs. Samson and Cairns took the opportunity at this meeting to present our evidence and views to Dr. Herzberg of the National Research Council. He was extremely interested in our upper atmosphere research in the vacuum ultraviolet

region in general and with our O_2 ionization results in particular. He was inclined to support our views and pointed out the importance in measuring the true ionization potential.

Two interesting papers on the photoionization of N_2 were presented, one by Codling and Madden of the N.B.S. and the other by Cook and Ogawa of the Aerospace Corporation. The Codling paper dealt with the absorption spectrum of N_2 as obtained using the radiation from the N.B.S. 180-MeV synchrotron while Cook's paper presented quantitative absorption cross sections. Where Cook's data overlapped with our data using the solar lines, there was good agreement.

On October 14 and 15, 1964, Drs. Samson and Cairns attended the 17th Annual Gaseous Electronics Conference in Atlantic City, New Jersey. The prime purpose of the visit was to present the paper entitled "Photoionization Threshold Potential of O_2 " as described earlier. Measurements of electron impact ionization of O_2 , presented by the group from General Dynamics/General Atomic, San Diego, allowed a comparison of the photon and electron impact techniques. An attempt to estimate the sensitivity of the electron beam technique was made in discussions with people such as Hagstrum and Simpson. Errors due to such processes as electron release when metastable neutral molecules are incident upon metal collectors were mentioned.

A theoretical paper given by Sewell, Texas Christian University, entitled "The Photoionization Cross Section of Neon" gave good agreement with the experimental work done at GCA under our current contract.

With regard to our present work, a discussion with Schiff suggested that in our measurements of atomic oxygen photoionization cross sections, account must be taken of the fact that about 20 percent of the neutral O_2 molecules issuing from the microwave discharge will be in metastable states.

Some discussions (with Wainfan) on proposed techniques for the measurement of the thickness of thin films emphasized the possibility of error due to the different sticking properties of coating materials on different surfaces. A review paper by Donahue, University of Pittsburgh, entitled "Radiation Transport and Gaseous Electronic Processes in the Upper Atmosphere" was limited to processes involving atomic H, O and Na such as the height profile of O and the H density on the day and night side of the Earth.